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(54) Abstract Title
Method of fabricating carbon nanotube field emitter using electrophoresis

(57) Method for fabricating a carbon nanotube field emitter by electrophoresis on a field emitter substrate 10' where the field emitter substrate includes cathodes arranged in stripes, a dielectric film formed with holes over the cathodes and metal gates formed with openings located over the holes of the dielectric film. The method comprises loading an electrode plate 23 and field emitter substrate 10' into an electrophoresis bath 21 containing a carbon nanotube suspension 22. Then a voltage is applied between the electrode plate and the cathodes of the field emitter substrate to deposit carbon nanotube particles at room temperature on the surfaces of the cathodes exposed through the holes of the dielectric film on the field emitter substrate. The field emitter substrate upon which the nanotubes have been deposited is then drawn out of the bath and heated. The nanotubes in the suspension may have a length between 0.1 and 1 micrometer and may be screened by field flow fractionation. The nanotube suspension may include a surfactant eg Tritron X-100, AOT and nitrates of $Mg(OH)_2$, $Al(OH)_2$ and $LA(OH)_3$ and be sonicated during the electrophoresis. The voltage applied may be in the range 1-1000 volts and may be applied for a duration between 1 second and 10 minutes. The nanotube may be deposited to a thickness of 0.01 to 0.5 micrometers and may be heated at a temperature of 150 to 500°C.

FIG. 7

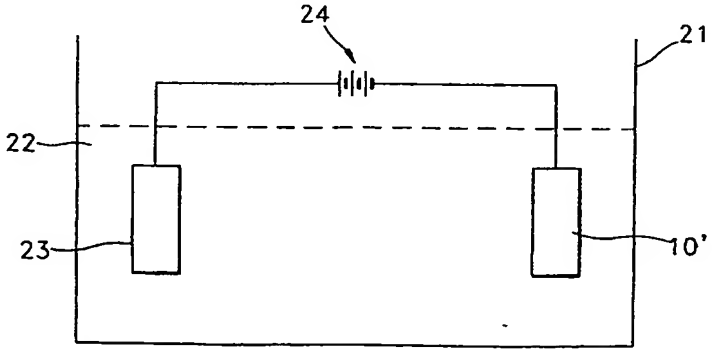

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FIG. 1 (PRIOR ART)

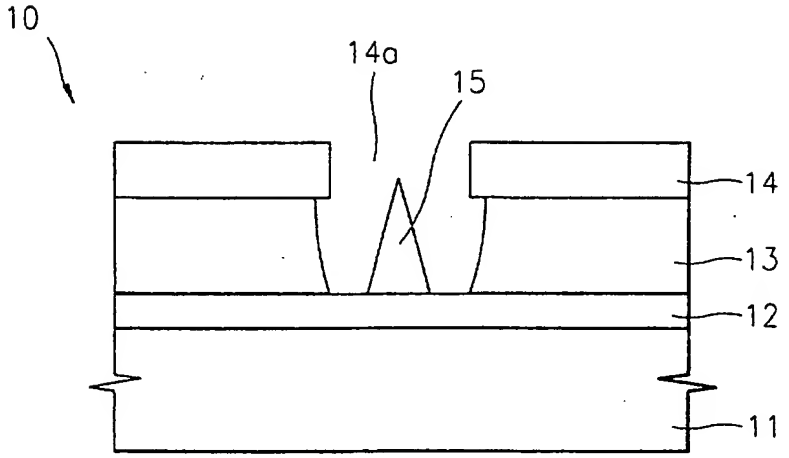


FIG. 2 (PRIOR ART)

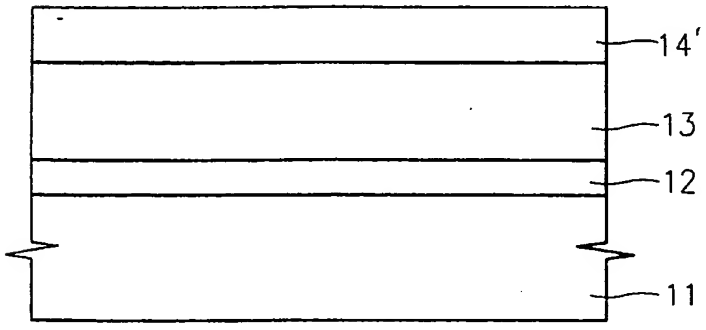


FIG. 3 (PRIOR ART)

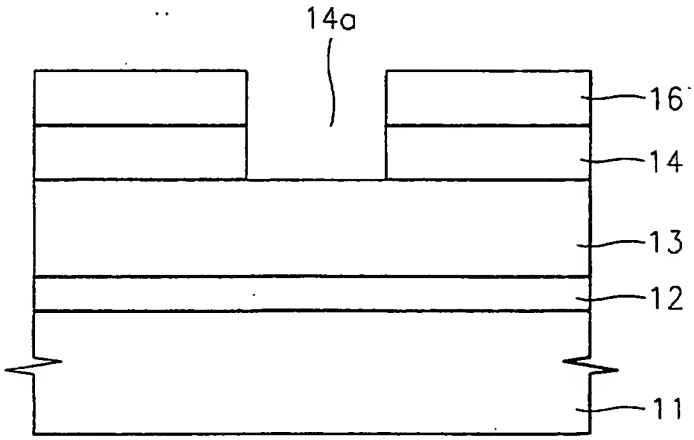


FIG. 4 (PRIOR ART)

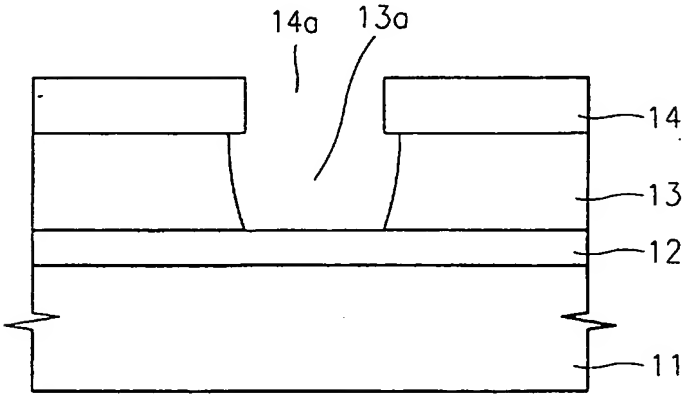
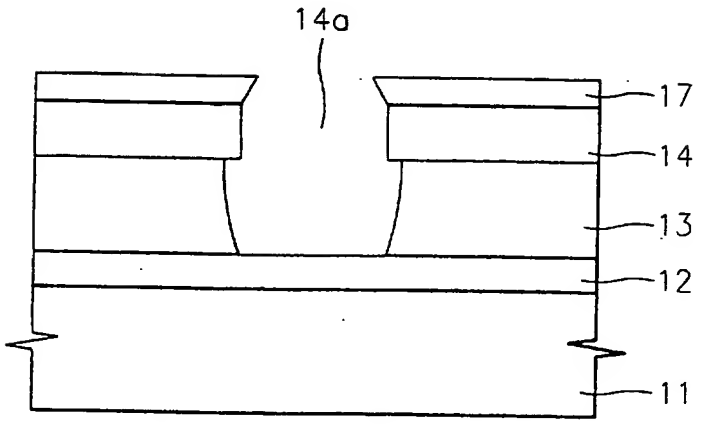


FIG. 5 (PRIOR ART)



FIGF. 6 (PRIOR ART)

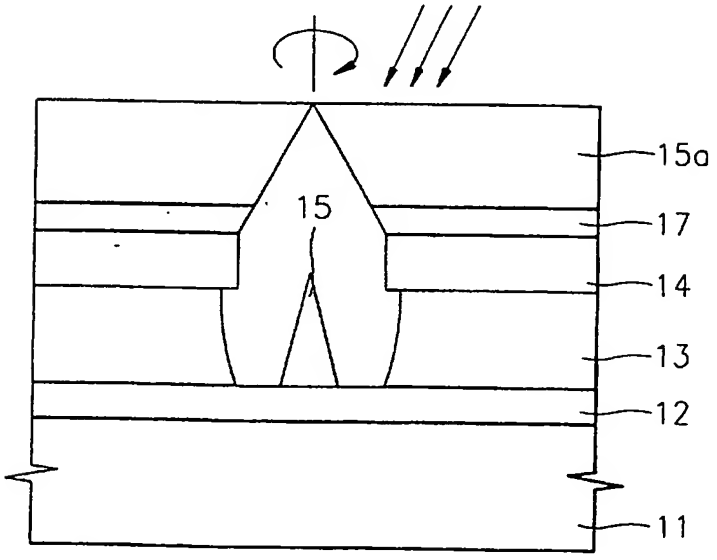


FIG. 7

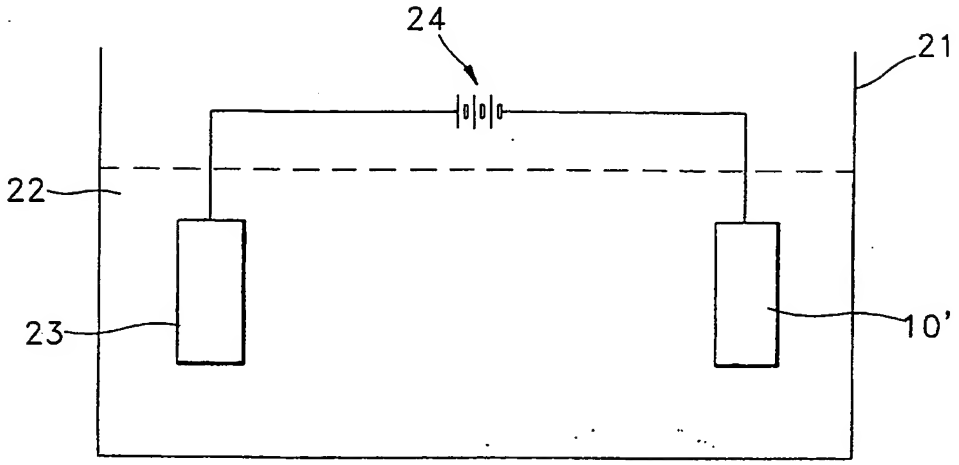


FIG. 8

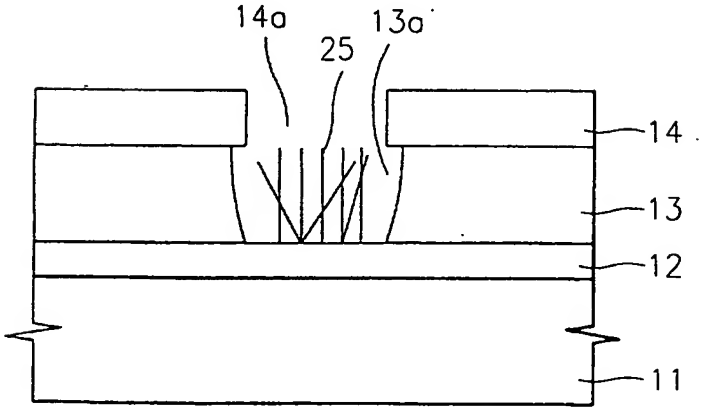


FIG. 9

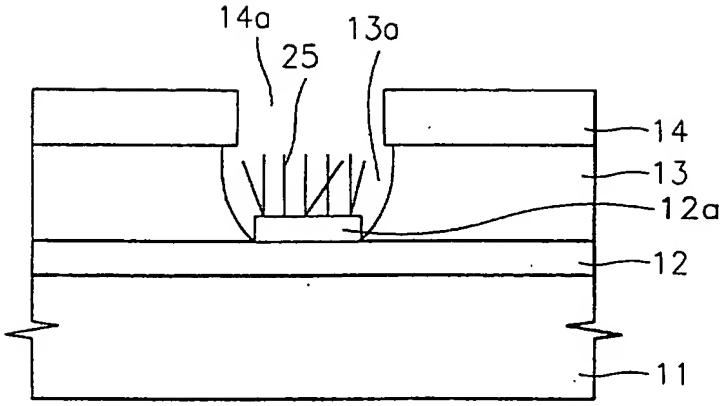


FIG. 10

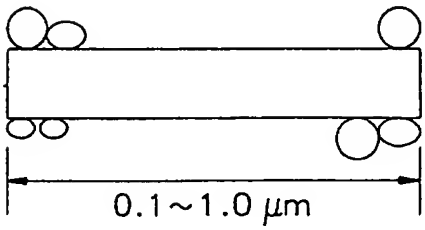
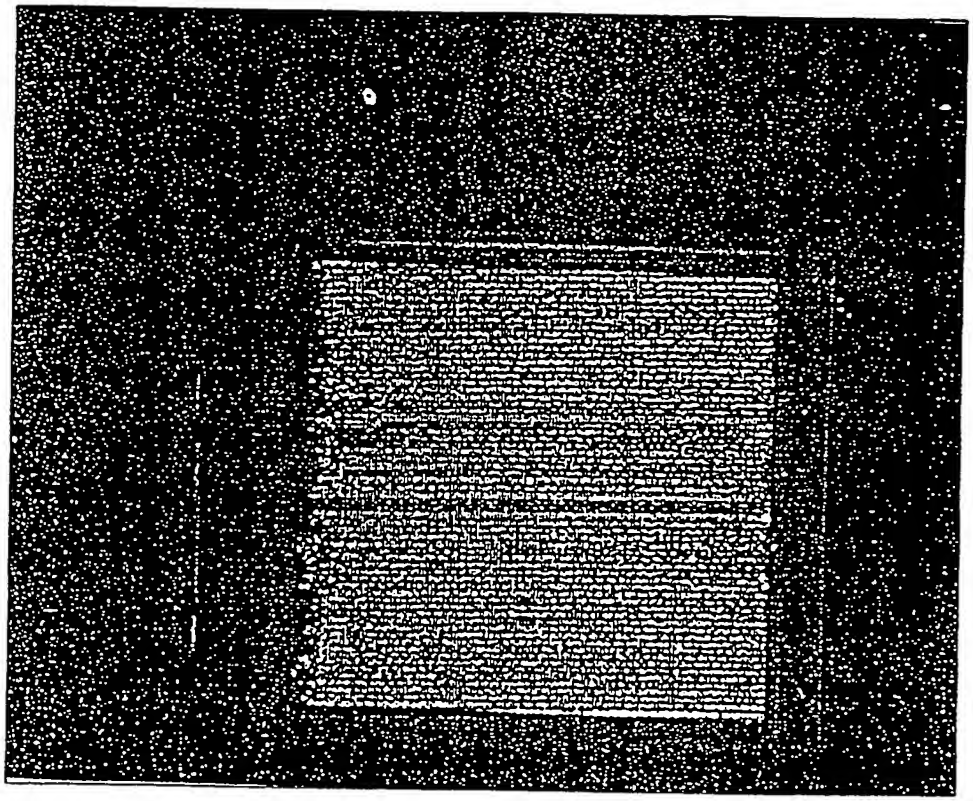


FIG. 11



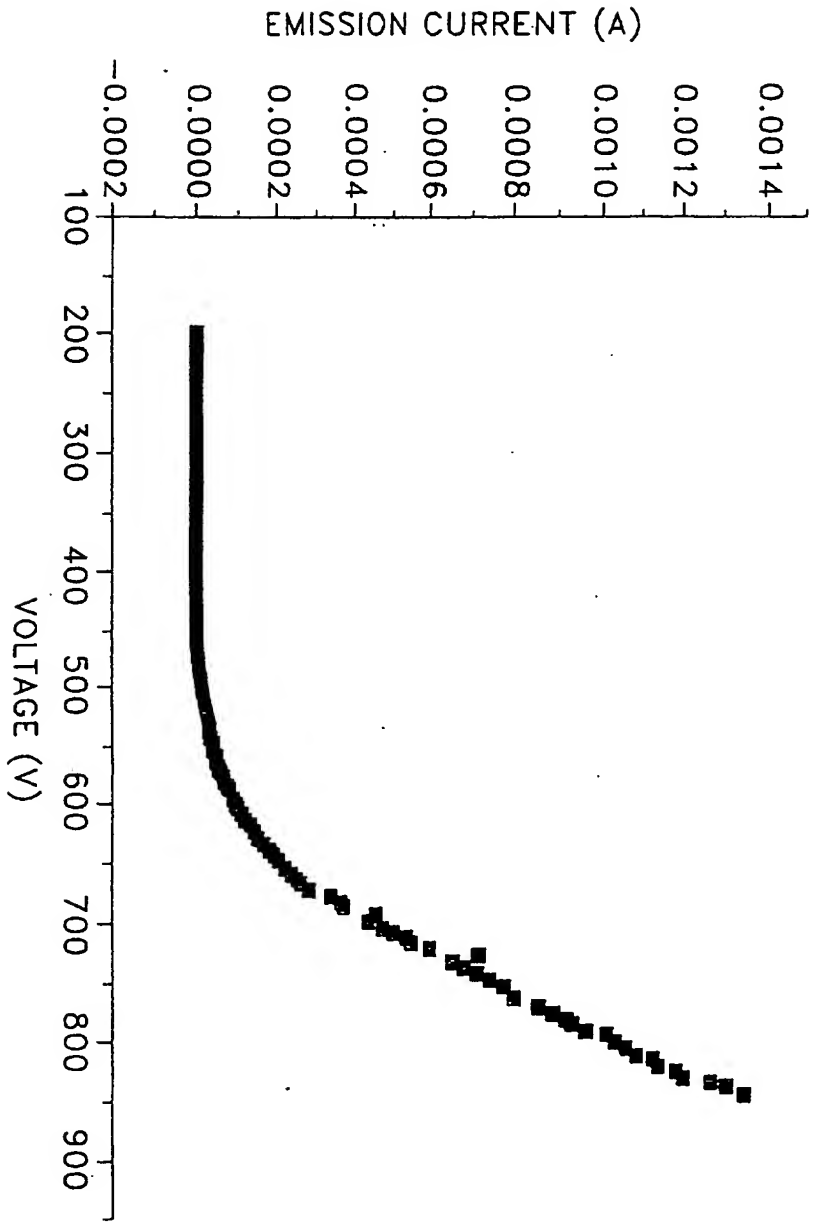

EMISSION CURRENT (A)
-0.0002
0.0000
0.0002
0.0004
0.0006
0.0008
0.0010
0.0012
0.0014
VOLTAGE (V)
100
200
300
400
500
600
700
800
900

FIG. 12

METHOD FOR FABRICATING CARBON NANOTUBE FIELD EMITTER BY ELECTROPHORETIC DEPOSITION

The present invention relates to a method for fabricating a field emitter for use in field emission displays, and more particularly, to a method for fabricating a carbon nanotube field emitter on electrodes of a field emitter substrate by electrophoretic deposition.

The use of field emitters as electron emitters for field emission displays is expected to dramatically increase in future generation flat displays. Field emitters emit electrons by creation of a strong electric field around the same. The current emission density of electrons is proportional to the intensity of the electric field produced around the field emitter, and the intensity of the electric field is influenced by the geometrical shape of the field emitter. Field emitters which act as electron emitters for field emission displays are usually formed in a cone shape with a sharp tip.

FIG. 1 is a sectional view of a conventional field emitter with a tip cone manufactured by a spindt technique. The conventional field emitter comprises a cathode 12 on a glass substrate 11, a sharp tip 15 for emitting electrons, which is arranged on the cathode 12, a dielectric film 13 patterned to surround the tip 15, and a gate 14 formed on the dielectric film 13 with an opening 14a above the tip 15, which allows for electron emission. In a field emission display, a plurality of cathodes are arranged in strips on a glass substrate.

A method for manufacturing the conventional field emitter in FIG. 1 for field emission displays by the spindt technique, which has been widely used, is set forth below.

FIGS. 2 through 6 are sectional views of successive stages of the method for fabricating the conventional field emitter in FIG. 1. Referring to FIG. 2, the electrode 12 is formed in a stripe on the glass substrate 11, and followed by the formation of the dielectric film 13 and a gate layer 14'. Next, as shown in FIG. 3, a photoresist mask 16 is formed on the gate layer 14' and the gate 14 with the opening 14a thereon, by photolithography. After lifting off the photoresist mask 16, the dielectric film 13 is etched using the gate 14 as an etching mask to produce a hole 13a in the dielectric film 13.

Then, as shown in FIG. 5, after depositing a sacrificial layer 17 on the gate 14, the structure is spun to grow the tip 15 with a high-melting point material by electron beam

deposition. Then, the sacrificial layer 17 and a by-product layer 15a deposited during the tip deposition are removed by etching, which results in the field emitter shown in FIG. 1.

However, the lifetime of the tip in a field emitter such as that shown in FIG. 1 is shortened due to the ionized gases used for deposition and nonuniform electric field distribution during operation. A material having a low work function, such as molybdenum (Mo), is needed to lower a driving voltage of a field emitter. However, the use of molybdenum as a material for the emitter tip does not secure a satisfactory lifetime of the tip as described above. To overcome this drawback, diamond and carbonic substances have been deposited to form emitter tips at high temperatures. However, this technique performed at high temperatures results in nonuniform coating properties of the product. Also, the use of diamond cause a problem that a large-area of the emitter cannot be coated.

According to the invention there is provided a method for fabricating a carbon nanotube field emitter by electrophoresis on a field emitter substrate including cathodes arranged in stripes on a substrate, a dielectric film formed with holes over the cathodes, and metal gates formed with openings located over the holes of the dielectric film, on the dielectric film, the method comprising: (a) loading an electrode plate and the field emitter substrate being spaced apart from one another into an electrophoresis bath containing a carbon nanotube suspension for the electrophoresis; (b) applying a predetermined bias voltage from a power supply between the electrode plate and the cathodes of the field emitter substrate to deposit at room temperature carbon nanotube particles on the surface of the electrodes exposed through the holes of the dielectric film; and (c) drawing the field emitter substrate on which the carbon nanotube particles have been deposited, out of the electrophoresis bath, and heating the field emitter substrate with carbon nanotube tips at a predetermined temperature.

The method of the invention uses electrophoretic deposition, in which emitter tips are formed of an ultra fine carbon nanotube having a low work function, which lowers a driving voltage of electrodes. The electrophoresis deposition at low temperatures avoids deterioration by ionization of residual gases during operation, thereby elongating the life of the emitters.

Preferably, for preparation of the carbon nanotube suspension used in the step (a), carbon nanotube particles having a length of 0.1 to 1 micrometer are screened by field-flow fractionation. Preferably, the carbon nanotube suspension used in the step (a) contains a surfactant selected from the group consisting of Tritron X-100, AOT and nitrates of

$Mg(OH)_2$, $Al(OH)_3$ and $LA(OH)_3$ and is sonicated during the electrophoresis. Also, in the step (b), the bias voltage applied between the electrode plate and the cathodes of the field emitter substrate may be in the range of 1 to 1000 volts. Preferably, the bias voltage is applied for 1 second to 10 minutes. Preferably, in the step (b), the carbon nanotube particles are deposited to a thickness of 0.01 to 0.5 micrometer. Preferably, in the step (c), the heating is performed at a temperature of 150 to 500°C.

Examples of the invention will now be described in detail, with reference to the accompanying drawings in which:

FIG. 1 is a sectional view of a conventional field emitter with a tip cone fabricated by a spindt technique;

FIGS. 2 through 6 are sectional views of successive stages of a method for fabricating the field emitter device in FIG. 1; and

FIG. 7 illustrates an electrophoresis bath which is utilized to fabricate a carbon nanotube field emitter device according to the present invention;

FIGS. 8 and 9 are sectional views illustrating methods for fabricating a carbon nanotube field emitter by electrophoretic deposition according to the present invention;

FIG. 10 illustrates a charged carbon nanotube particle which allows a suspension for electrophoresis; and

FIG. 11 illustrates an emission image of a field emission display adopting carbon nanotube field emitter arrays of the present invention; and

FIG. 12 is an I-V curve illustrating the field emission properties of the field emitter according to the present invention.

A method for fabricating a carbon nanotube emitter device by electrophoresis according to the present invention will now be described with reference to FIGS. 7 and 10. In the drawings, like reference numerals are used to refer to like elements throughout.

The field emitter substrate shown in FIG. 4, which refers to the structure immediately before formation of micro tips, is loaded into an electrophoresis bath 21 shown in FIG. 7. In particular, for the field emitter substrate 10', a plurality of cathodes 12 are arranged in strips on a glass substrate 11, and a dielectric film 13 is formed with holes 13a over the cathodes 12. Next, metal gates 14 with openings 14a which are located over the holes 13a of the dielectric film 13, are formed to expose the surface of the cathodes 12.

Then, carbon nanotubes are uniformly deposited onto the obtained field emitter substrate 10', onto the surface of the cathodes 12 exposed through the holes 13a, by electrophoretic deposition at room temperature, which is set forth below.

Initially, as shown in FIG. 7, the field emitter substrate 10' is loaded into the electrophoresis bath 21 containing a carbon nanotube suspension 22. An electrode plate 23 is also installed in the electrophoresis bath 21 being spaced apart from the field emitter substrate 10'. The cathode of a DC (or AC) power supply 24, which is installed outside of the electrophoresis bath 21, is connected to the cathodes 12 of the field emitter substrate 10', and the anode of the DC power supply 24 is connected to the electrode plate 23. Then, a bias voltage of 1 to 1000 volts is applied from the DC power supply 24 between the electrode plate 23 and the cathodes 12 of the field emitter substrate 10'.

Then, as a positive voltage of the DC power supply 24 is applied to the electrode plate 23, carbon nanotube particles charged by positive ions in the carbon nanotube suspension 22 migrate to and are attached to the exposed cathodes 12 of the field emitter substrate 10', which results in carbon nanotubes 25 as shown in FIG. 8.

FIG. 9 illustrates another embodiment of the carbon nanotube emitter according to the present invention, in which a thin film 12a is deposited on the cathodes 12 of the field emitter substrate 10' and carbon nanotubes 25 are formed on the thin film 12a. In the present embodiment, the carbon nanotube particles are deposited in a similar manner as in the embodiment illustrated in FIG. 8, and thus a detailed explanation thereof is not repeated.

The carbon nanotubes 25 for the field emitter according to the present invention are prepared by an arc discharge or laser technique. The particles of the carbon nanotube have a length in the order of several tens of nanometers to several tens of micrometers, and contain metal particles used as a catalyst and carbonic impurities. The carbon nanotube particles are reacted with a strong acid such as HNO_3 and H_2SO_4 to remove impurities therefrom, cut to have appropriate lengths, and subjected to sedimentation and field-flow fractionation using a separator to screen carbon nanotube particles having a length of approximately 1 micrometers for use in preparation of a suspension for the electrophoresis. The carbon nanotube suspension contains a surfactant such as Tritron X-100, bis(1-ethylhexyl)sodium sulfosuccinate, commonly known as AOT, and nitrates of $Mg(OH)_2$, $Al(OH)_3$ or $La(OH_3)$ and is sonicated during the electrophoresis, in which carbon nanotube particles are charged with positive or negative charges as shown in FIG. 10. Here, the

intensity of the electric field and time for which the electric field is applied define the thickness of the carbon nanotube layer. A higher voltage level and a longer voltage application time result in a thicker carbon nanotube layer.

For applications to a diode, an electric field having opposite charges to those on the surface of carbon nanotube particles is applied to exposed electrode surface of a field emitter substrate for selective deposition of carbon nanotube particles thereon. Meanwhile, for applications to a triode having gates, which is illustrated as the embodiments of the present invention, a weak positive electric field is applied to the gates 14 while a positive electric field is applied to the electrodes 12 of the field emitter substrate 10', which avoids deposition of carbon nanotube particles on the gates 14. In particular, as previously described, the electrode plate 23 is connected to the anode of the DC power supply 24 and the cathodes 12 of the field emitter substrate 10' are connected to the cathode of the DC power supply 24. As a positive potential is applied to the gates 14, the gates 14 repel positive ions in the carbon nanotube suspension 22 at the surface, while the exposed cathodes 12 of the field emitter substrate 10', which are connected to the cathode of the DC power supply 24, pull positive ions of the suspension through the holes 13a. As a result, the carbon nanotubes 25 are deposited only on the entire exposed surface of the cathodes 12, not on the gates 14 of the field emitter substrate 10'. At this time, carbon nanotube particles are almost vertically aligned near the openings 14a of the gates 14, which allows the carbon nanotube particles to smoothly migrate through the holes 13a to the cathodes 12, and thus the carbon nanotubes 25 can be deposited in order as shown in FIGS. 8 and 9.

After the deposition of carbon nanotube particles by electrophoresis, low-temperature heating is performed to sustain the deposition of the carbon nanotubes 25 on the cathodes 12 and ensure easy removal of impurities which are incorporated into the field emitter during the deposition. Accordingly, the field emitters shown in FIGS. 8 and 9, which have carbon nanotubes 25 having a low work function, are completed.

FIG. 11 illustrates an emission image of a field emission display adopting carbon nanotube field emitter arrays according to the present invention, and FIG. 12 is an I-V curve illustrating the field emission properties of a field emitter according to the present invention.

A conventional field emitter has a very strong emission current density, so that its operational lifetime is shorted by ionization of residual gases within a vacuum area. However, by forming the field emitter tips with carbon nanotube particles by electrophoretic

deposition as in the present invention, the emission current density with respect to applied voltages may be maintained to be low as shown in FIG. 12, which results in an enhanced durability by avoiding the ionization of residual gases, and in turn a longer lifetime of the field emitter.

As described above, the present invention provides a method for fabricating a carbon nanotube field emitter by electrophoresis, which allows for a field emitter with a large area and a selective emitter deposition for a triode. Since the carbon nanotube particles have a low work function, a driving voltage of electrodes can be lowered. Also, the overall fabrication process is performed at low temperatures, which reduces manufacturing cost and prevents ionization of residual gases, enhancing the durability of the field emitter.

While this invention has been particularly shown and described with reference to preferred embodiments thereof, it will be understood by those skilled in the art that various changes in form and details may be made therein without departing from the scope of the invention as defined by the appended claims.

CLAIMS

1. A method for fabricating a carbon nanotube field emitter by electrophoresis on a field emitter substrate including cathodes arranged in stripes on a substrate, a dielectric film formed with holes over the cathodes, and metal gates formed with openings located over the holes of the dielectric film, on the dielectric film, the method comprising:

(a) loading an electrode plate and the field emitter substrate being spaced apart from one another into an electrophoresis bath containing a carbon nanotube suspension for the electrophoresis;

(b) applying a predetermined bias voltage from a power supply between the electrode plate and the cathodes of the field emitter substrate to deposit at room temperature carbon nanotube particles on the surface of the electrodes exposed through the holes of the dielectric film; and

(c) drawing the field emitter substrate on which the carbon nanotube particles have been deposited, out of the electrophoresis bath, and heating the field emitter substrate with carbon nanotube tips at a predetermined temperature.

2. The method of claim 1, wherein for preparation of the carbon nanotube suspension used in the step (a), carbon nanotube particles having a length of 0.1 to 1 micrometer are screened by field-flow fractionation.

3. The method of claim 1, wherein the carbon nanotube suspension used in the step (a) contains a surfactant selected from the group consisting of Tritron X-100, AOT and nitrates of $Mg(OH)_2$, $Al(OH)_3$ and $LA(OH)_3$ and is sonicated during the electrophoresis.

4. The method of claim 1, wherein in the step (b), the bias voltage applied between the electrode plate and the cathodes of the field emitter substrate is in the range of 1 to 1000 volts.

5. The method of claim 4, wherein the bias voltage is applied for 1 second to 10 minutes.

6. The method of claim 1, wherein in the step (b), the carbon nanotube particles are deposited to a thickness of 0.01 to 0.5 micrometer.

7. The method of claim 1, wherein in the step (c), the heating is performed at a temperature of 150 to 500°C.

8. A method for fabricating a carbon nanotube field emitter by eletrophoresis, substantially as described herein with reference to the accompanying drawings.

Application No: GB 0010071.9 **Examiner:** Rachel Foxon
Claims searched: all **Date of search:** 25 September 2000

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.R): H1D

Int Cl (Ed.7): H01J

Other: Online: WPI, EPODOC, JAPIO, INSPEC

Documents considered to be relevant:

Category	Identity of document and relevant passage		Relevant to claims
A,P	EP 0989579	Lucent Technologies (see esp col 9 lines 42-45)	-
A,P	EP 0951047	Canon Kabushiki (see esp embodiments 6,14 and col 14 lines 45-47)	-

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.